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Abstract

MgB₂ /Fe wires with 10 at. % excess Mg produced by in situ powder-in-tube processing were compared to normal stoichiometric MgB₂ /Fe wires prepared by the same method. It was found that the critical current density J_c and the irreversibility field (H_{irr}) were significantly enhanced for MgB₂ /Fe wires with excess Mg. The transport J_c for 10 at. % Mg excess samples sintered at 800 degrees C, measured at a field of up to 14 T, increased by a factor of 2 compared to that for the normal MgB₂ wires. The best J_c results for the 10 at. % Mg excess sample were obtained by heating the sample at 600 degrees C for 1 h; the J_c at a field of 8 T and at temperature of 10 K reached 3104 A/cm². The detailed analysis of the effect of excess Mg on the microstructures, the J_c , and the H_{irr} , of MgB₂ /Fe wires are presented in this paper.

Keywords

Excess, addition, MgB₂, wires, enhanced, critical, current, density

Disciplines

Engineering | Physical Sciences and Mathematics

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Excess Mg addition MgB₂/Fe wires with enhanced critical current density

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MgB₂/Fe wires with 10 at. % excess Mg produced by *in situ* powder-in-tube processing were compared to normal stoichiometric MgB₂/Fe wires prepared by the same method. It was found that the critical current density (J_c) and the irreversibility field (H_{irr}) were significantly enhanced for MgB₂/Fe wires with excess Mg. The transport J_c for 10 at. % Mg excess samples sintered at 800 °C, measured at a field of up to 14 T, increased by a factor of 2 compared to that for the normal MgB₂ wires. The best J_c results for the 10 at. % Mg excess sample were obtained by heating the sample at 600 °C for 1 h; the J_c at a field of 8 T and at temperature of 10 K reached 3×10^4 A/cm². The detailed analysis of the effect of excess Mg on the microstructures, the J_c , and the H_{irr} of MgB₂/Fe wires are presented in this paper. © 2008 American Institute of Physics. [DOI: 10.1063/1.2909203]

I. INTRODUCTION

Since the discovery of magnesium diboride (MgB₂) superconductor,¹ it has been extensively studied by many research groups that aim for high current applications. Intensive research has been performed to fabricate MgB₂/Fe wires/tapes with high critical current density J_c .^{2–6} Recently, kilometer-long MgB₂ wires have been fabricated.⁷ Some research groups have produced small magnets using MgB₂ wire.⁸ However, most of these efforts are focused on the improvement of the high field J_c and H_{c2} by broad chemical doping. Little attention has been paid in improving the connectivity up until now. Among the chemically doped materials, nano-SiC, nanocarbon, and carbon nanotube doped samples have reached the dirty limit and demonstrated the highest H_{c2} and high field J_c .^{2–5} However, their low field J_c remains unchanged, and, in some cases, it is even degraded. High field range is very important to many MgB₂ applications that require large critical current densities. Thus, the connectivity problem responsible for a relatively low J_c in a high field range must be addressed. In our previous paper,⁹ we discussed the effect of excess Mg on the superconducting properties, especially on the magnetic J_c and H_{c2} of bulk samples. In this paper, the microstructure, the transport J_c , and H_{irr} of normal stoichiometric and excess Mg MgB₂/Fe wires sintered at different temperatures were compared. We demonstrate that enhancement in transport J_c can be achieved by a combination of excess Mg and optimal processing.

II. EXPERIMENTAL PROCEDURE

MgB₂/Fe wire samples were prepared by an *in situ* reaction method.⁹ Magnesium (Mg, 99%) and amorphous bo-

ron (B, 99%) powder were mixed for fabrication of MgB₂/Fe wires. For the excess Mg addition samples, a mixture of Mg and B powder with a ratio of 1.1:2 was prepared. The well-mixed powders were formed into MgB₂/Fe wires by the standard powder-in-tube technique.¹⁰ The powder-in-tube composites were drawn down to thin wires with diameters of 0.8 mm. All the samples were then sealed in iron tubes and sintered at 600 °C for 1 h at 700 to 900 °C for 30 min under argon flow. All samples were characterized by x-ray diffraction (XRD), the results were analyzed by using the Rietveld refinement XRD to determine the a and c lattice parameters and the MgO content. Transport J_c of wire samples was measured using pulsed and direct current (dc) methods at a magnetic field range of up to 14 T and temperatures of 4.2, 10, and 20 K. The magnetoresistivity $\rho(H, T)$ was measured with H applied perpendicular to the current direction using the four probe method in the temperature range from 4.2 to 300 K and the field range from 0 to 9 T. The irreversibility fields H_{irr} and H_{c2} can be deduced using the criteria of 0.1 and 0.9 of $\rho(H, T)$, respectively.

III. RESULTS AND DISCUSSION

Figure 1 shows the field dependence of pulse current (PC) and dc transport J_c at 4.2, 10, and 20 K for the normal stoichiometric and the 10 at. % excess Mg MgB₂/Fe wires (the overall diameter is $\Phi=0.8$ mm): (a) PC and dc transport J_c at 4.2, 10, and 20 K for samples heat treated at 800 °C, (b) PC transport J_c at 10 and 20 K for all samples, and (c) dc transport J_c at 20 K for samples treated at 600 °C for 1 h, and 700 and 800 °C for 30 min. Only dc transport J_c values at a high field region and at 4.2 and 20 K are shown in the Figs. 1(a) and 1(c), because it is difficult to precisely measure J_c values at low fields due to the heat generation at current contacts. The PC transport J_c values at the high field region are precise, which is confirmed by dc measurements

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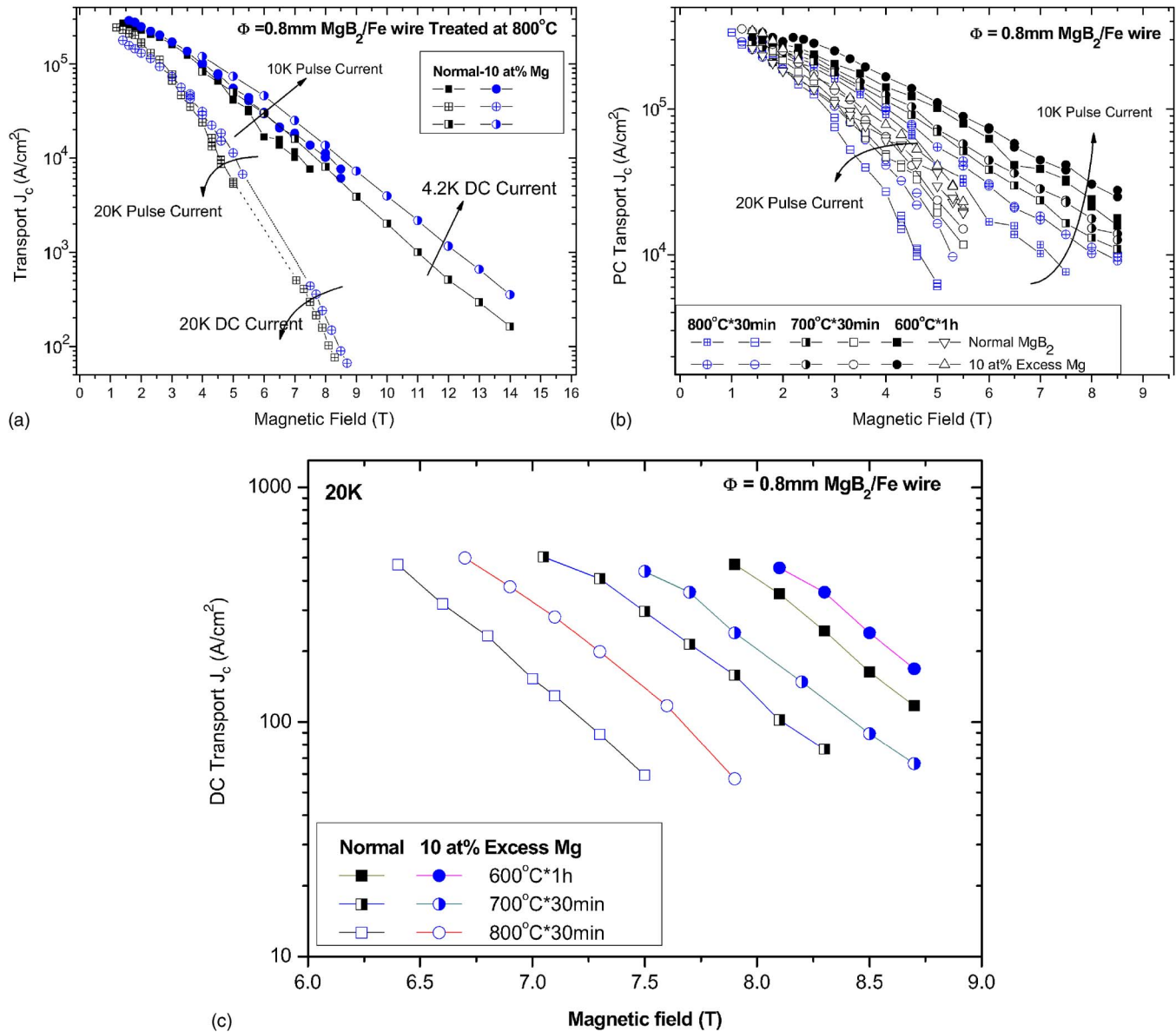


FIG. 1. (Color online) The field dependence of pulse current (PC) and direct current (dc) transport J_c at 4.2, 10, and 20 K for normal stoichiometric and 10 at. % excess Mg $\Phi = 0.8$ mm MgB_2/Fe wires: (a) PC and dc transport J_c at 4.2, 10, and 20 K for samples treated at 800°C , (b) PC transport J_c at 10 and 20 K for all samples, and (c) dc transport J_c at 20 K for samples treated at 600°C for 1 h and at 700 and 800°C for 30 min.

at 4.2 K and at high fields of up to 14 T as shown in Fig. 1(a), and dc measurements at 20 K and up to 8.7 T, as shown in Fig. 1(c). The best J_c results for the 10 at. % Mg excess samples are obtained for the samples heat treated at 600°C for 1 h; the J_c at a field of 8 T and at temperature 10 K reaches $3 \times 10^4 \text{ A}/\text{cm}^2$. This may be caused by the improved grain connectivity and the enhanced flux pinning induced by the addition of excess Mg (Ref. 9) and the low sintering temperature. The transport J_c at a field of up to 14 T for 10 at. % Mg excess samples increased by a factor of 2 compared to that for the normal MgB_2 samples.

Figure 2 shows the XRD patterns of the superconducting cores of Fe sheathed (a) normal stoichiometric MgB_2 and (b) 10 at. % Mg excess wire samples treated from 600 to 900°C . There is no indication of the MgB_4 phase; however, peaks correspond to the unreacted crystalline Mg and impurity phase MgO can be observed in both normal and

10 at. % excess Mg wire samples sintered at 600°C . In contrast to the reaction in bulk samples (Fig. 3), in which Mg and B completely reacted after sintering at 650°C for 0.5 h, the complete reaction temperature between Mg and B in wire samples increased. For MgB_2 wire samples with normal stoichiometric MgB_2 , the complete reaction temperature is 700°C , while for the wire sample with excess Mg, this temperature is increased to 800°C . It is also noted that the Bragg peaks corresponding to MgB_2 become sharper and stronger with the increase in the sintering temperature. The grain size of MgB_2 increases with the sintering temperature, as calculated from full width at half maximum (FWHM) (Table I). This different behavior of the MgB_2 phase formation in the bulk and Fe sheathed wire samples is probably due to the fact that the bulk sample was sealed in an Fe tube with a large volume; therefore, the Mg vapor pressure during sintering may be slightly lower than that of wire sintering.

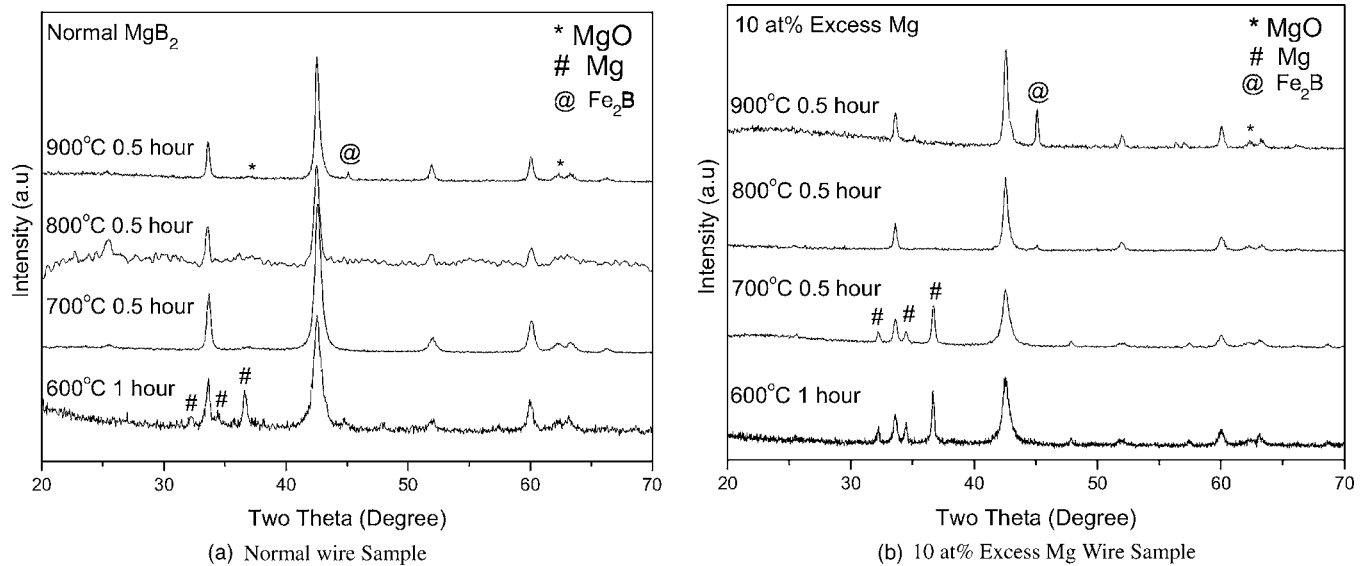


FIG. 2. The x-ray diffraction patterns of the superconducting cores of Fe sheathed wires treated from 600 to 900 °C: (a) normal stoichiometric MgB_2 samples and (b) 10 at. % Mg excess samples.

The excess of Mg could increase the Mg vapor pressure in the Fe tube, thus speeding up the formation of MgB_2 and suppressing the large crystal formation of MgB_2 by generating more nuclei for crystallization.

Figures 4 and 5 show the scanning electron microscopy (SEM) images of normal wire samples and 10 at. % Mg excess wire samples treated at (a) 600 °C, (b) 700 °C, (c) 800 °C, and (d) 900 °C. The SEM observation shows that there is a large amount of spherical holes in the cores of both normal wire samples and 10 at. % Mg excess samples, which is the nature of *in situ* MgB_2 processing. Most of the holes are close to the size of the Mg particles in the mixed $\text{Mg}+2\text{B}$ powder precursor. These holes could be produced by the volume reduction in the $\text{Mg}+2\text{B}$ reaction, but they could also be partially attributed to the evaporation of the Mg particles during the sintering of the wires. It can be seen

from Figs. 4 and 5 that the MgB_2 particle size for the normal samples is slightly larger than that for the 10 at. % excess Mg samples. This is understandable because the excess Mg provided more melted or evaporated Mg to react with B particles during sintering. More MgB_2 nucleation seeds would be formed and the MgB_2 grain size would be smaller. Another interesting phenomenon we would like to point out, is that the edge of normal MgB_2 particles is sharp, while the edge of particles in excess Mg samples looks smooth, and the particles are aggregated together. The connectivity of MgB_2 particles in the excess Mg samples is much better. The melted excess Mg may play an important role in cleaning the grain boundary and healing the microcracks as well.

Since our wires are very thin ($\Phi=0.8$ mm), it is difficult to remove the Fe sheath without damaging the core. We can use the bulk samples' magnetoresistance results for compar-

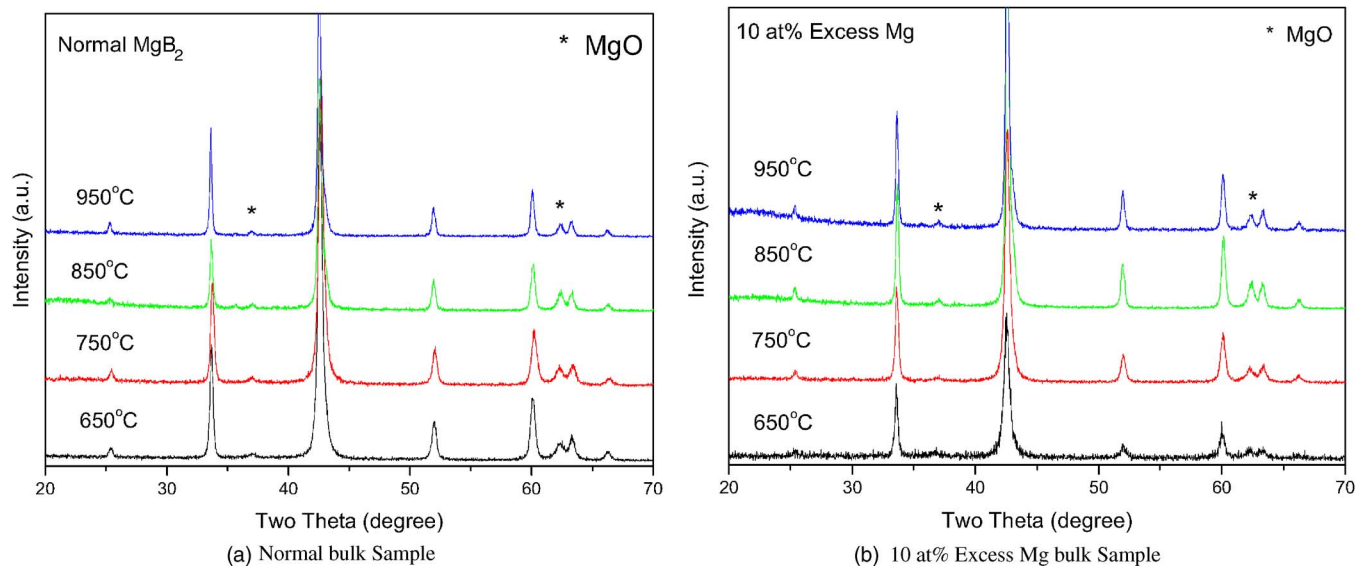


FIG. 3. (Color online) The x-ray diffraction patterns of bulk samples treated from 650 to 950 °C: (a) normal stoichiometric MgB_2 samples and (b) 10 at. % Mg excess samples.

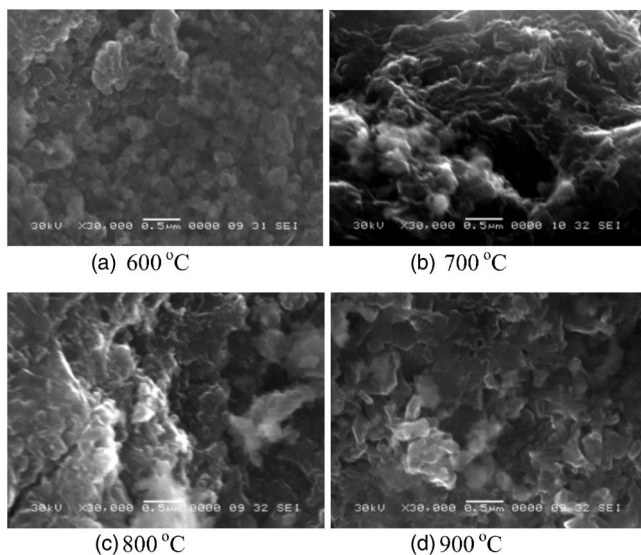
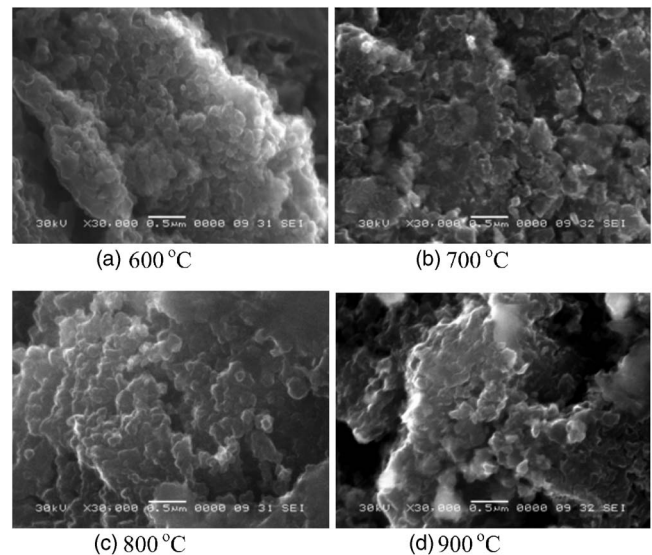
TABLE I. Comparison of FWHM, irreversibility field (H_{irr}), and transport J_c (10^4 A/cm 2) at 20 K, 4 T and at 10 K, 8 T for normal MgB $_2$ and 10 at. % excess Mg MgB $_2$ wires sintered at different temperatures.

Samples	T ($^{\circ}$ C) and time (h)	FWHM (110) (deg)	H_{irr} (T) (100 A/cm 2 , 20 K)	J_c (10^4 A/cm 2)	
				(20 K, 4 T)	(10 K, 8 T)
Normal MgB $_2$ wire	600 and 1 h	0.610	>8.7	6.3	2.2
	700 and 0.5 h	0.570	8.1	4.9	1.3
	800 and 0.5 h	0.48	7.2	2.4	0.57
10 at. % excess Mg wire	600 and 1 h	0.810	>8.7	7.8	3.0
	700 and 0.5 h	0.784	8.4	5.8	1.8
	800 and 0.5 h	0.520	7.6	4.2	1.1

ing and refereeing, although preparing the condition between wire and bulk samples was different. Some unreacted Mg was found in the wire samples, and unreacted Mg can significantly affect the resistivity.^{17,18} The difference between the superconducting properties of the normal MgB $_2$ and the excess Mg wire samples can be estimated according to our results and those of Refs. 17 and 18. Figure 6 shows an irreversibility field (H_{irr} , circle symbols) and an upper critical field (H_{c2} , square symbols) as a function of temperature for (a) normal and (b) 10 at. % Mg excess MgB $_2$ bulk samples sintered at temperatures ranging from 650 to 950 $^{\circ}$ C. It can be seen that both H_{irr} and H_{c2} of the excess Mg samples treated at 650 $^{\circ}$ C are significantly improved in comparison to the normal samples treated at the same temperature. The H_{c2} for the 10 at. % Mg excess samples sintered at 650 $^{\circ}$ C reaches 8.7 T at 25 K, while H_{c2} for the normal samples is just 6.6 T. In contrast, the H_{c2} and H_{irr} showed little difference between the 10 at. % Mg excess samples and the normal samples when the sintering temperature is higher than 750 $^{\circ}$ C.

Figure 7 shows the resistivity versus temperature for the normal MgB $_2$ samples [Fig. 7(a)] and the excess Mg samples [Fig. 7(b)] sintered at temperatures ranging from 650 to 950 $^{\circ}$ C. By comparing Fig. 7(a) with 7(b), it is found that

the resistivity of these samples shows an opposite trend to that of samples sintered at temperatures lower than 750 $^{\circ}$ C. That is, the resistivity of the 10 at. % excess Mg samples is higher than that of the normal samples. This suggests that the enhancement in H_{c2} is a result of scattering from impurities in B sites. The O substitution for B in the excess Mg sample can explain the strong enhancement in H_{c2} . According to the dual reaction model proposed by the authors' group, easy and optimal doping can be achieved when the substitution by the doping reagent takes place at the same time as MgB $_2$ formation.³ Sintering at 650 $^{\circ}$ C creates an ideal condition for oxygen incorporation into the lattice, as 600–650 $^{\circ}$ C is the optimal temperature range for MgB $_2$ formation from Mg and amorphous B powders in the *in situ* process.^{2,3,10} We speculate that, at elevated sintering temperature, the Mg(B,O) $_2$ alloying phase decomposes to form precipitates which do not contribute to an increase in H_{c2} , but act as pinning sites to improve J_c , which we have explained in our previous paper.⁹ The resistivity of the 10 at. % excess Mg sample is lower than that of the normal sample when the sintering temperature is higher than 750 $^{\circ}$ C, as shown in Fig. 7. The residual resistivity ratio, defined as $\rho(300\text{ K})/\rho(40\text{ K})$, and the active area fraction (A_F) of each sample were listed in Fig. 7.

FIG. 4. SEM images of normal samples treated at (a) 600 $^{\circ}$ C, (b) 700 $^{\circ}$ C, (c) 800 $^{\circ}$ C, and (d) 900 $^{\circ}$ C.FIG. 5. SEM images of 10 at. % Mg excess samples treated at (a) 600 $^{\circ}$ C, (b) 700 $^{\circ}$ C, (c) 800 $^{\circ}$ C, and (d) 900 $^{\circ}$ C.

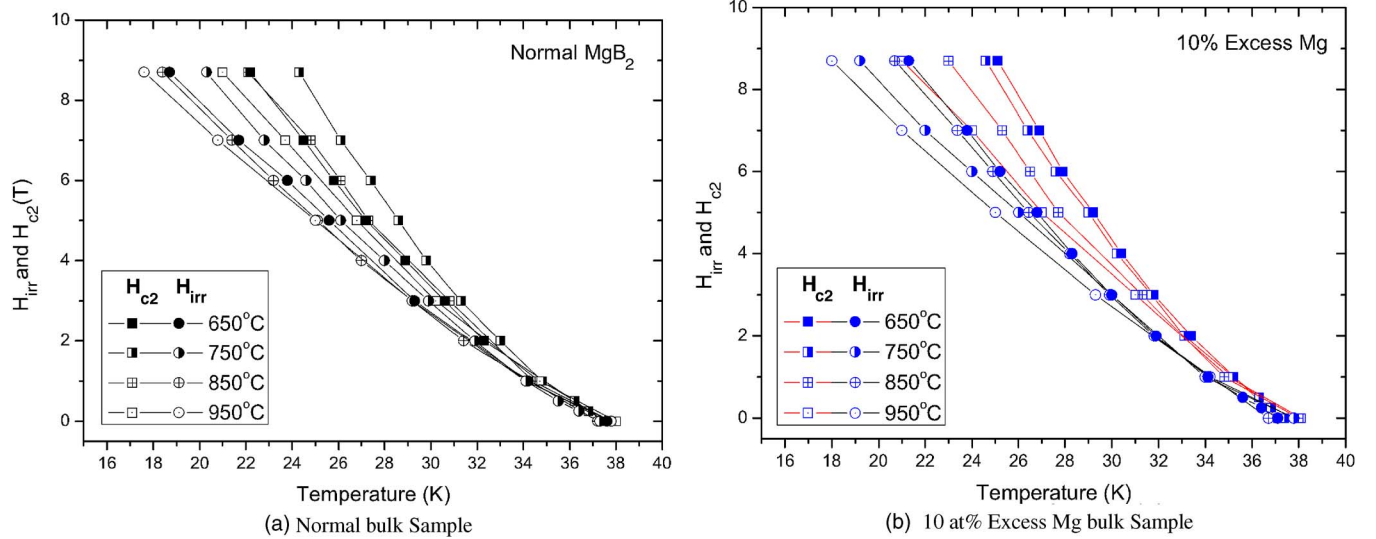


FIG. 6. (Color online) Irreversibility field (H_{irr} , round symbols) and upper critical field (H_{c2} , square symbols) as a function of temperature for (a) normal and (b) 10 at. % Mg excess MgB_2 bulk samples sintered at a temperature range of 650–950 °C.

The A_F was estimated from a modified version of Rowell's formulas,¹² as $A_F = \Delta\rho_{ideal}/[\rho(300\text{ K}) - \rho(40\text{ K})]$, where $\rho(T)$ is our experimentally measured resistivity at temperature T . The connectivity in the Mg excess samples is better than that in the normal samples except for the 650 °C treated samples. Both A_F of 650 °C treated normal and excess Mg samples are the same=0.1. This may due to the competition results of Mg vaporizing and grain size (grain boundary scattering) since a lower temperature results in less Mg vaporizing, and a smaller grain size results in more electron scattering. The connectivity of the high temperature treated samples is better than that of the low temperature treated samples.

The influence of the flux pinning and connectivity on J_c in the MgB_2/Fe wire samples is very complicated.¹³ It is well known that low temperature sintering results in small grain size and grain distortion (shown in our recent Raman spectrum results,¹⁴ which lead to more grain boundaries and

more point defect pinning centers shown in our recent result¹⁵), thereby enhancing the flux pinning. However, more grain boundaries will also increase the normal-state resistivity. In our experiment, we found that excess Mg can decrease the particle size and grain size of MgB_2 as well. Therefore, it will further enhance the flux pinning. Moreover, excess Mg decreases the content of MgO impurity⁹ and reduces the microcracks,^{11,16} which will significantly improve the connectivity. Table I shows the comparison of FWHM, irreversibility field (H_{irr}), and transport J_c (10^4 A/cm^2) at 20 K, 4 T and at 10 K, 8 T for normal MgB_2 and 10 at. % excess Mg MgB_2 wires sintered at different temperatures. It can be seen that the low temperature sintered excess Mg samples have the highest J_c , although there is still some unreacted Mg in the wire that is heat treated at 600 °C for 1 h, as shown in Fig. 2(b). Excess Mg addition appears to be a promising

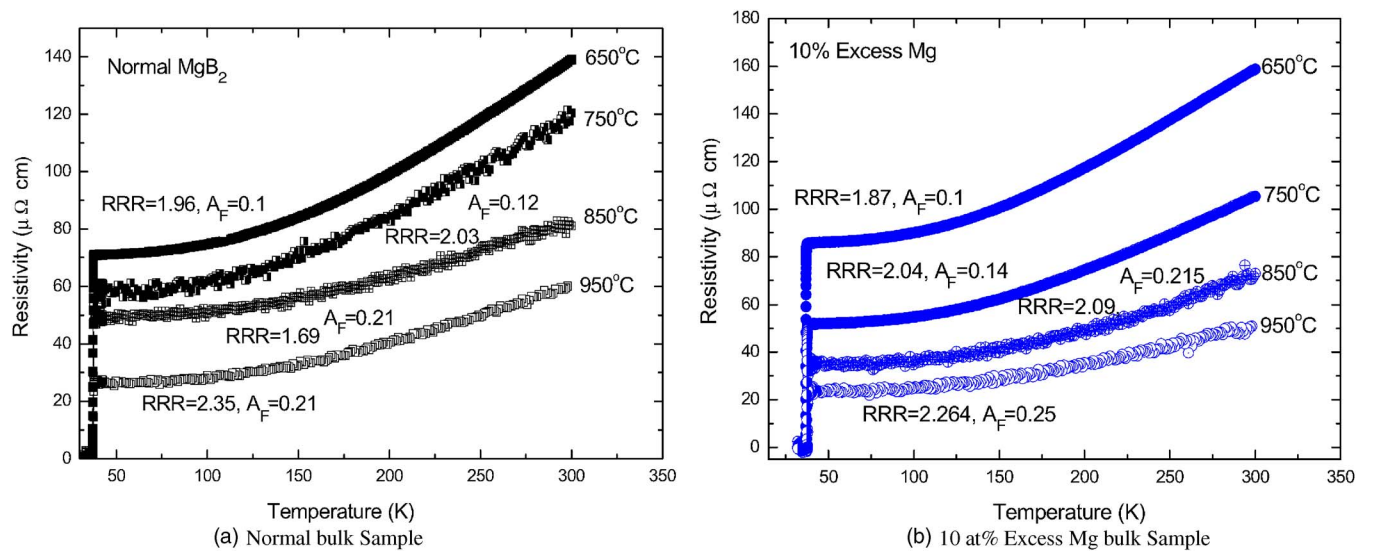


FIG. 7. (Color online) The normal-state resistivity as a function of temperature for (a) normal and (b) 10 at. % Mg excess MgB_2 samples processed at a temperature range of 650–950 °C.

method to enhance J_c of MgB_2 wires. We believe that this approach still has a huge potential in further J_c enhancement through process optimization.

IV. CONCLUSIONS

We have investigated the effect of Mg excess on the microstructure and the J_c of MgB_2/Fe wires. By comparing to normal MgB_2/Fe wire samples, the excess Mg samples show smaller grain size and lower MgO content, thus significantly enhancing the critical current density and irreversibility field. The enhancements in J_c and H_{irr} are strongly dependent on the sintering temperature. The highest J_c results for the 10 at. % Mg excess sample were obtained in the wire samples that were heat treated at 600 °C for 1 h; the J_c at a field of 8 T and at temperature 10 K reached 3×10^4 A/cm², and the H_{irr} at 20 K is larger than 8.7 T.

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